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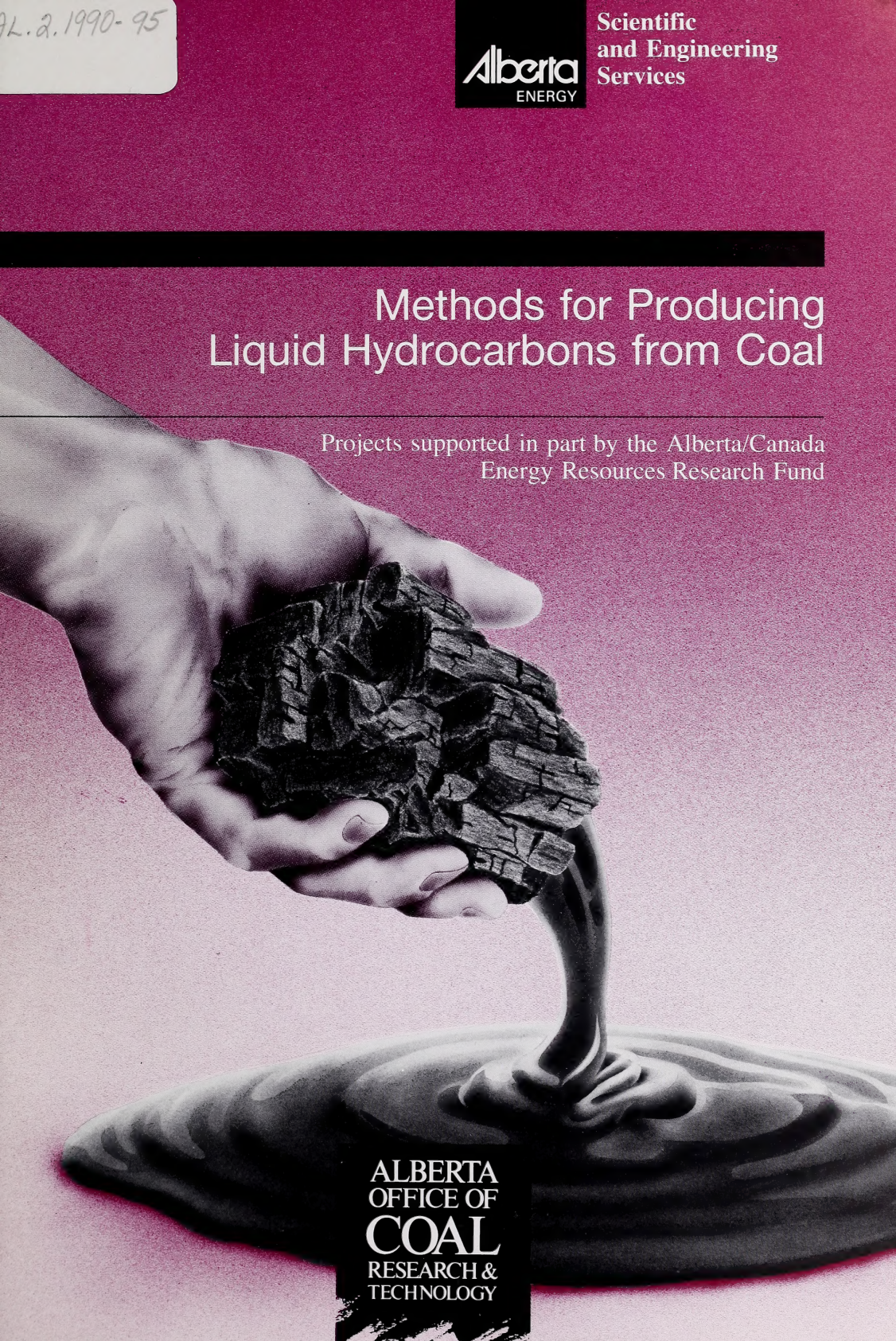
Alberta ENERGY

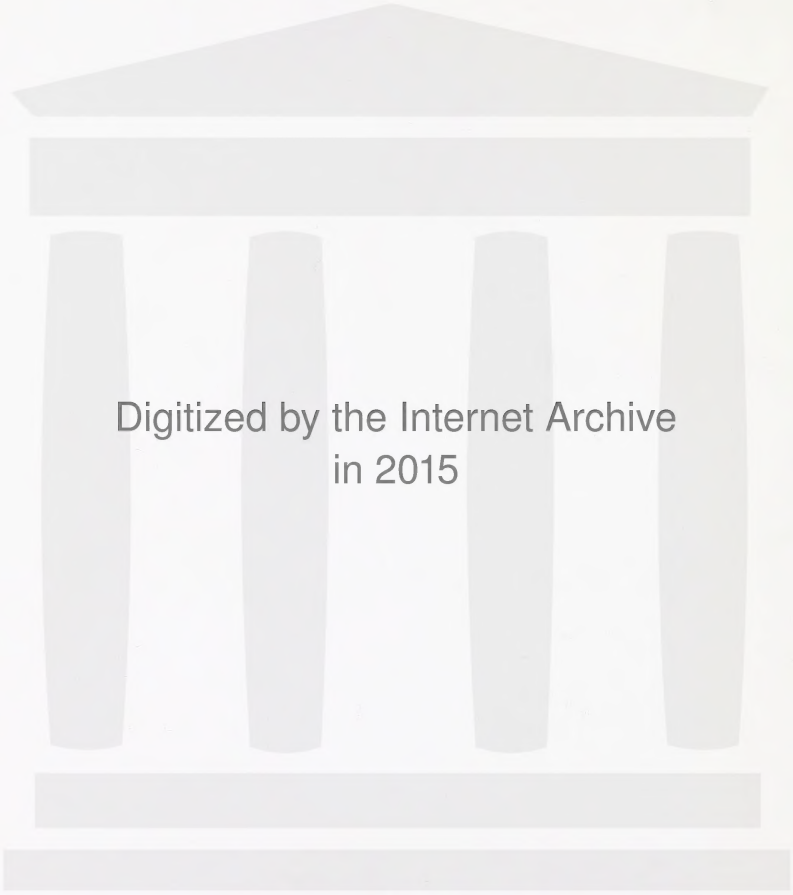
Scientific and Engineering Services

Methods for Producing Liquid Hydrocarbons from Coal

Projects supported in part by the Alberta/Canada Energy Resources Research Fund



ALBERTA OFFICE OF COAL RESEARCH & TECHNOLOGY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Methods for Producing Liquid Hydrocarbons from Coal

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by the Alberta/Canada
Energy Resources
Research Fund

1990
Edmonton

Alberta
ENERGY
Scientific and Engineering
Services and Research Division

Pub. No. I/300

ISBN 0-86499-651-9

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Foreword

Since 1976, numerous projects have been initiated in Alberta by industry and by academic research institutions which are aimed at better utilization of Alberta's energy resources.

These research, development and demonstration efforts were funded by the Alberta/Canada Energy Resources Research Fund (A/CERRF), which was established as a result of the 1974 agreement on oil prices between the federal government and the producing provinces.

Responsibility for applying and administering the fund rests with the A/CERRF Committee, made up of senior Alberta and federal government officials.

A/CERRF program priorities have focused on coal and conventional energy resources, as well as energy conservation and renewable energy. Program administration is provided by staff within the Scientific and Engineering Services and Research Division of Alberta Energy.

In recognition of the importance of coal to Alberta's economy, the Alberta Office of Coal Research and Technology was established in 1984 within Alberta Energy and Natural Resources (now Alberta Energy). Its primary purpose is to encourage the development and application of new technologies related to Alberta coals. The Office provides funding contributions to research and development projects in industry, academic institutions and other research establishments and monitors their progress in an overall program of improving the production, transportation and marketability of Alberta coals.

In order to make research results available to industry and others who can use the information, highlights of studies are reported in a series of technology transfer booklets. For more information about other publications in the series, please refer to pages 16 and 17.

Methods for Producing Liquid Hydrocarbons from Coal

In January 1980, funding from the Alberta/Canada Energy Resources Research Fund (A/CERRF) was provided to the Coal and Hydrocarbon Processing Department of the Alberta Research Council (ARC) to begin a research program on coal liquefaction.

In the early stages of this work, subbituminous coals from Alberta's major deposits were tested under conditions that were typical of several known liquefaction processes. These screening experiments identified promising processes and process conditions best suited to Alberta coals, as well as the relative reactivity of Alberta coals in these processes. This led to detailed evaluations in semi-continuous and continuous-flow bench-scale reactor studies. From this stage of the work evolved a recognition that one promising method for producing liquid hydrocarbons from coal involved reacting coal with bitumen, heavy oil or liquid derived from bitumen under hydrogenation or solvation conditions. This led to a major research effort in the field of co-processing, and one Alberta company currently plans to construct a commercial-scale co-processing plant partly based on ARC experience with this coal liquefaction method.

The co-processing route to coal liquids was described in 1988 in the technology transfer publication titled "Co-processing Studies of Alberta Subbituminous Coals."

Meanwhile, ARC scientists continued to study more traditional routes for liquefying coal. This included hydropyrolysis as an alternative method for producing hydrocarbon liquids and a carbon-enriched char that can be combusted for electric power generation.

Concurrently, researchers at the University of Alberta experimented with alternative methods for producing liquid hydrocarbons from coal. One of these involved supercritical gas extraction of coal, while the other directly employed Alberta's abundant natural gas as a hydrogenating agent.

The findings of these studies, as well as those of a relevant waste water treatment investigation, are described here.

Initial Coal Liquefaction Studies at Alberta Research Council

To distinguish it from coal pyrolysis and co-processing, coal liquefaction involves the use of a solvent to convert coal from a solid to a liquid slurry (solubilization), followed by catalytic hydrogenation of the slurry at high temperatures and pressures. At the time of the initial screening studies, coal liquefaction technologies were at various stages of development in Japan, Great Britain, the United States and the Federal Republic of Germany. In particular, the ARC investigations concentrated on the I.G. Farben process. Initial experiments with this process revealed that individual coals were quite different in their susceptibility to liquefaction under identical reaction conditions, and the type of solvent had a marked effect on conversion efficiency and the amount of hydrogen converted to water.

Subsequent batch studies were carried out with three types of subbituminous coals in 1 000 ml autoclaves at a maximum temperature of 475°C and a maximum pressure of 41.7 MPa. Anthracene oil was used as solvent. Regardless of reaction conditions, it was found that the decreasing order of reactivity was subbituminous C > A > B, and conversion rates varied from 67 to 95 per cent.

Experiments using the three types of subbituminous coals were repeated in a mini-autoclave (130 ml capacity) which allowed short residence time reactions to occur. When conditions typical of the I.G. Farben process were used, it was found that the relative reactivity of the coals was as observed earlier, although conversion rates were lower. They ranged from 53 to 66 per cent. When the experiments were repeated using carbon monoxide-steam in place of hydrogen, conversion rates were higher (75 to 82 per cent) at lower reaction temperatures (400°C versus 460°C). Both sets of experiments involved an evaluation of various reaction conditions, including reaction temperature, pressure and time, as well as catalyst and solvent type.

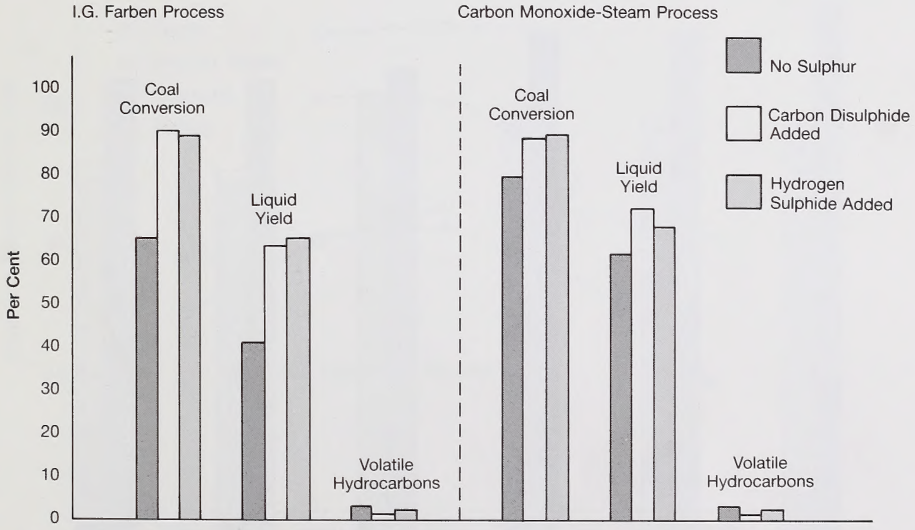
Similarly, the larger 1 000 ml autoclave was used again to study the effects of a dispersed catalyst in a process developed by the Dow Chemical Company. Higher rates of conversion were observed for the Dow hydrogen/dispersed-catalyst system. They ranged from 90 to 96 per cent for the three types of coal, versus 84 to 95 per cent for the carbon monoxide-steam process. Of three catalysts tried in the hydrogen/dispersed-catalyst experiments, potassium molybdate was superior to iron salts and cobalt sulphate.

Subsequently, subbituminous coal from the Highvale mine was tested in the Dow process at the Dow research centre in Midland, Michigan. Yields of liquid products from a 300 ml reactor ranged from 49 to 53 per cent.

During the initial two years of coal liquefaction studies, other investigations were launched to provide support services for these process evaluations. For example, coal chemistry and coal petrography studies were used to gain some understanding of the factors that contributed to the relative reactivity of subbituminous coals. Measurements of the empirical molecular weight of coal, as well as the fraction of hydrocarbon-yielding volatile products, the oxidation state of the volatile carbon structure, the mean vitrinite reflectance and the molecular fragment representing a potential source of hydrocarbons in solvolytic liquefaction reactions were useful in both liquefaction and pyrolysis studies. In particular, petrography was investigated as a potential method for predicting the yields of gaseous and liquid products from coal liquefaction.

Investigations were also begun during this period to develop instrumental methods for characterizing the products of coal liquefaction and providing analytical tools useful for process control. For example, thermogravimetric analysis (TGA) was shown to be capable of simulating a conventional proximate analysis of coal, and both gas chromatography and TGA were tried as methods for identifying and quantitatively measuring components of coal-derived liquids. Also, in anticipation of the need to perform larger scale liquefaction reactions, several engineering aspects were reviewed or studied. For example, a state-of-the-art review was made of heat transfer principles applicable to coal slurries, and a report was prepared to stress the importance of coal slurry flow characteristics (rheology) on the efficiency of liquefaction reactions.

Coal Conversion and Product Distribution in I.G. Farben and Carbon Monoxide-Steam Processes with and without Hydrogen Sulphide or Carbon Disulphide Added



(Source: Effect of Added H_2S or CS_2 on the Liquefaction of Alberta Subbituminous Coals in I.G. Farben and CO/Steam Process Types, Lewkowicz, L., K. Badree, B. Ignasiak and M.P. du Plessis, Coal Research Department, Alberta Research Council, 1983)

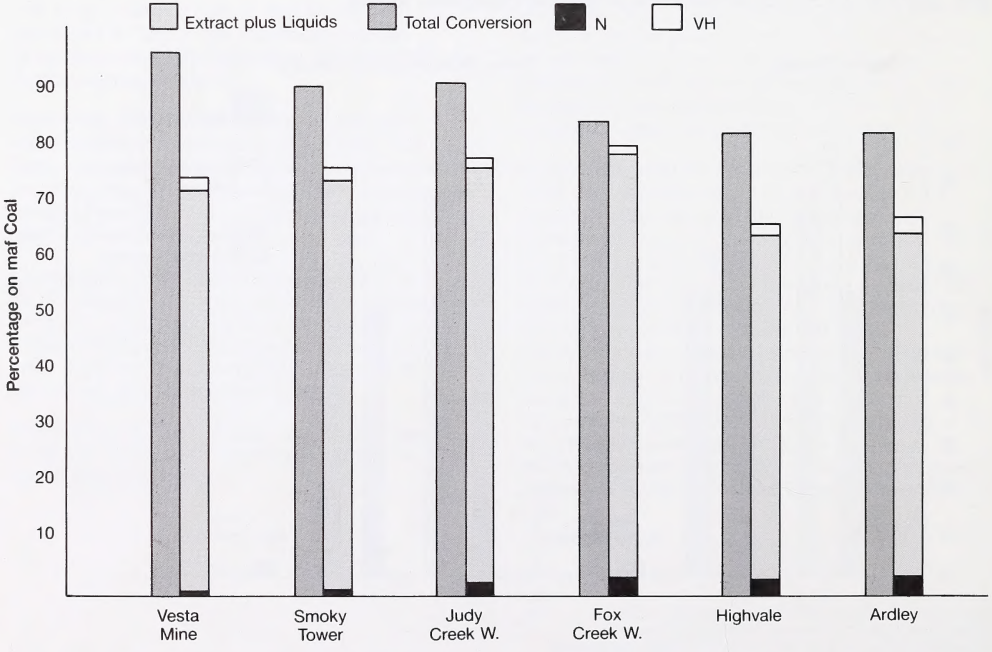
As coal liquefaction experiments continued, the influence of hydrogen sulphide/carbon disulphide (H_2S/CS_2) on coal conversion and the yield of liquid products was investigated for both the I.G. Farben process and the carbon monoxide-steam process. Using subbituminous coal from the Highvale mine, anthracene oil as the solvent, and a 1 000 ml autoclave as the reaction vessel, it was found that hydrogen sulphide alone or in combination with carbon disulphide caused the coal conversion to rise by approximately 32 per cent and the liquid yield to rise by 55 per cent in the I.G. Farben experiments. In the case of the carbon monoxide-steam experiments, the results were not quite as dramatic, but both the coal conversion and the liquid product yield showed substantial increases (11 per cent and 16 per cent, respectively) when compared with experimental runs in the absence of sulphur-containing compounds. In both the I.G. Farben and the carbon monoxide-steam experiments, H_2S/CS_2 caused a drop in the volatile hydrocarbon content of the reaction products.

Meanwhile, experiments were continued to evaluate various Alberta subbituminous coals in several liquefaction processes. For example, in the carbon monoxide-steam process, coal from the Vesta mine produced the highest conversion rates (95 per cent) of six coals tested in this process. The other coals were from Smoky Tower, Judy Creek, Fox Creek, Highvale and Ardley. The Fox Creek coal, however, gave the highest yield of useful conversion products. The relative behaviour of these same coals was evaluated in the dispersed-catalyst process. Also, some tests were performed in a 35 ml mini-autoclave to achieve short "heat up" times for each of the liquefaction processes.

By 1984, this body of work had established the optimum reaction conditions in a 1 000 ml batch reactor for each of the processes and each of nine subbituminous coals. This was supplemented by some experiments in the mini-autoclave. The nine coals were from two coal formations. The coals and their formations were:

Conversion of Coals and Product Distribution in Carbon Monoxide/Steam Reaction:

Reaction conditions: 50 g maf coal; 125 g anthracene oil; 1 000 psi CO; 34 g H_2O; 2.5 g potassium carbonate; 400°C; 30 mins; VH = Volatile Hydrocarbons; N = Naphtha



(Source: Evaluation of Subbituminous Coals of Alberta: Reaction of Ardley, Judy Creek and Fox Creek Coals with Carbon Monoxide and Steam, Gawlak, M., D. Carson, N. Shatilla and H. Wasylyk, Coal Research Department, Alberta Research Council, 1983)

Paskapoo Formation - Fox Creek, Judy Creek, Ardley, Highvale and Smoky Tower.

Horseshoe Canyon Formation - Tofield, Vesta, Pickardville and Battle River

The studies showed that Horseshoe Canyon coals were more reactive than Paskapoo coals. The average conversion values of coal from Highvale, Ardley, Judy Creek, Fox Creek and Smoky Tower ranged between 78 and 86 per cent, whereas the conversion rates for coals from Pickardville, Battle River, Vesta and Tofield were from 93 to 95 per cent.

It was apparent that the dispersed-catalyst process produced the highest conversion rates, and Vesta coal was the most reactive.

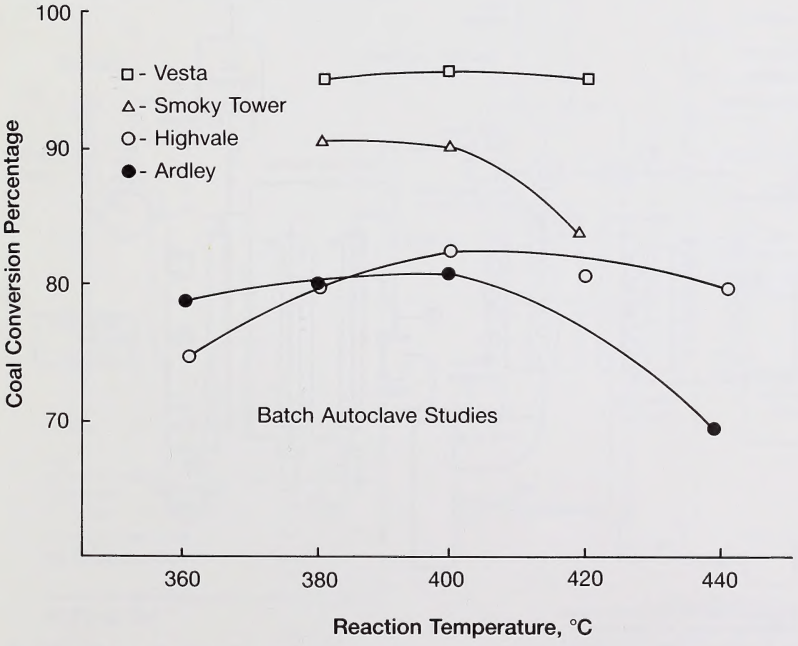
Bench-Scale Liquefaction

During 1984 and 1985, a 2-kg/h continuous-flow bench-scale liquefaction unit was used to liquefy Highvale and Vesta coals in a dispersed-catalyst process involving various catalysts and single- or two-stage processing. The range of experimental conditions was as follows:

Gas:	Hydrogen
Solvent:	Anthracene oil and process-derived liquids
Coal:	Highvale and Vesta (27-30 per cent, daf basis)
Catalyst:	Potassium molybdate, iron oxide and alumina-supported catalysts
Additive:	Dimethyldisulphide
Pressure:	20.7 MPa
Temperature:	400 to 470°C (first reactor) 425 to 470°C (second reactor)
Residence time:	25 to 70 min.
H_2 flowrate:	1.2 to 1.6 standard m^3/kg daf coal
Reactors:	1 and 2 litres

Results from the single-stage processing revealed that conversion rates in excess of 90 per cent were possible for both Vesta and Highvale coals, but only low yields (27 and 40 per cent, respectively) of low-quality oils were obtained. In an attempt to overcome this, two-stage processing was tried, but both the quality and yields remained low.

Coal Conversion vs. Reaction Temperature in Carbon Monoxide/Steam Process



(Source: Comparative Autoclave Liquefaction Studies of Alberta Subbituminous Coals — Final Report, Lewkowicz, L., R. Lott, S.K. Chakrabartty and B. Ignasiak, Coal Research Department, Alberta Research Council, 1984)

At this juncture, direct liquefaction experiments were terminated so that more of Alberta Research Council's resources could be used to continue the co-processing liquefaction work carried out in parallel with these studies. As noted earlier, this body of work was described in a previous technology transfer booklet.

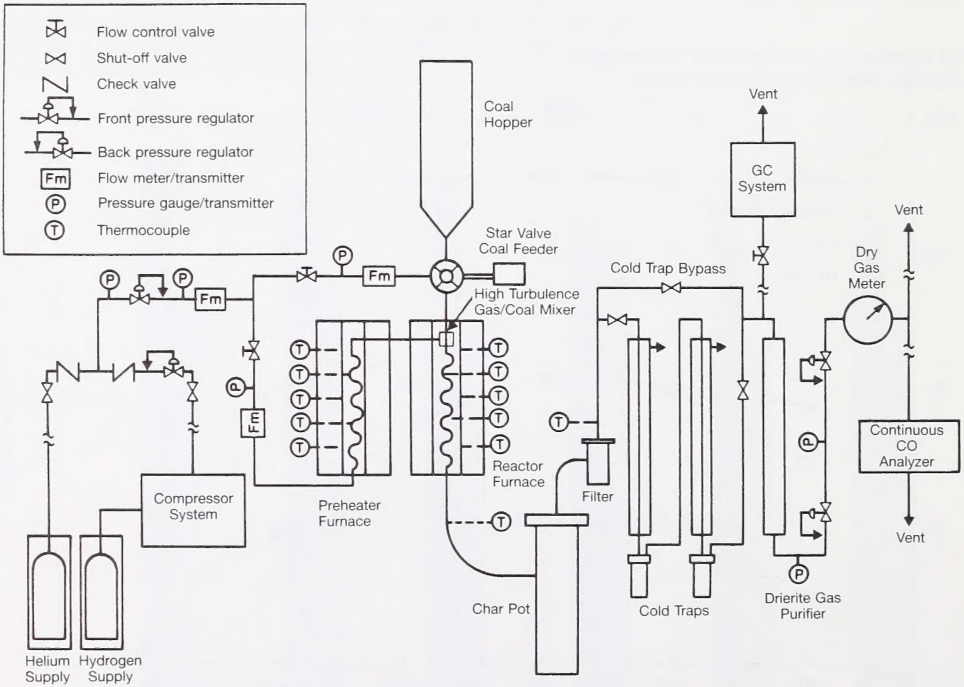
Pyrolysis and Hydropyrolysis Studies at Alberta Research Council

Concurrently with the direct liquefaction investigations at ARC, a program was launched to evaluate 10 subbituminous coals in four pyrolysis/hydropyrolysis processes. These systems are evolutionary forms of pyrolysis or "destructive distillation," which has long been used in the production of coke.

Pyrolysis is defined as a chemical reaction, initiated by heat, in the partial or complete absence of air. When coal is pyrolyzed, the following four types of products are formed: (1) a solid residue called a char or coke; (2) heavy organic liquids called tars or oils; (3) a watery liquid called liquor; and (4) gas. The characteristics and distribution of the products vary with each coal and are considered to define its "pyrolytic properties." Generally, two types of pyrolysis or coal carbonization reactions are recognized. They are high temperature carbonization (at approximately 950°C) and low temperature carbonization (at approximately 550°C).

In recent years, attention has shifted away from using pyrolysis to produce coke or char and toward capture of some of the volatile components in coal before the char is used as a solid fuel. This results in the formation of both gaseous and liquid products. Pyrolysis systems designed to produce liquids from coal and carried out in a hydrogen atmosphere are known as hydropyrolysis or

Coal Flash Pyrolysis/Hydropyrolysis System Schematic



(Source: Flash Pyrolysis/Hydropyrolysis of Alberta Subbituminous Coals: Design, Construction, Operation and Initial Results of a High Pressure 1-5 kg/hour Bench Unit, Gangwal, S.K. and J. Mendiuk, Coal Research Department, Alberta Research Council, 1983)

hydrocarbonization processes. If a catalyst is present, the process is called catalytic hydropyrolysis. Another variant, known as flash pyrolysis/ hydropyrolysis, refers to systems in which coal is heated to 450°C or higher in a fraction of a second in an inert/hydrogen atmosphere.

The initial work in this pyrolysis program involved tests of subbituminous coal from the Highvale mine in a flash hydropyrolysis process developed by Cities Service Research and Development Company in the U.S.A. These bench-scale tests were carried out in a 0.9 kg/h reactor at temperatures as high as 807°C. Under these conditions, 43 per cent of the coal carbon was converted to liquid and gaseous hydrocarbons. Seventeen per cent of this converted carbon appeared as liquid products.

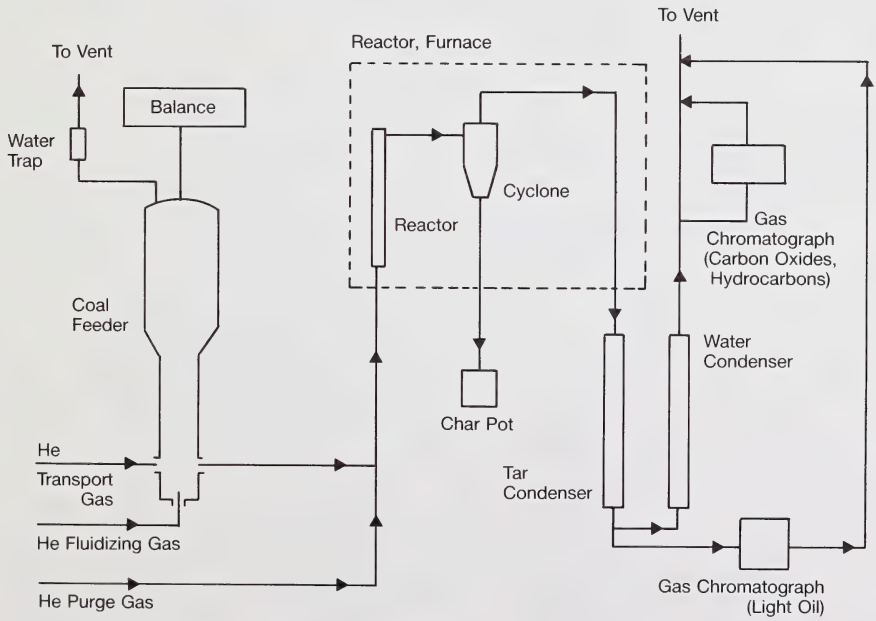
Subsequently, a laboratory-scale pyrolyzer and a bench-scale unit capable of processing up to 5 kg/h of coal were built at ARC. The bench-scale pyrolyzer was used to process coal in a continuous stream of hydrogen at pressures from 1 to 200 atmospheres and at temperatures of 500 to 900°C. The laboratory-scale unit was an entrained-flow reactor capable of handling 1 to 10 g/h of coal at atmospheric pressure. It was used to screen a variety of coals to determine those suitable for detailed studies in the bench-scale pyrolyzer.

Eventually, 10 coal samples from seven coal fields were evaluated. In one set of experiments, a blend was made of all the coals; the blend was then pyrolyzed in the entrained-flow reactor at atmospheric pressure. Conversion of this blend to volatiles increased with pyrolysis temperature from 24 to 34 per cent at 550°C to 47 to 55 per cent at 800°C. The maximum liquid hydrocarbon yields were 14 to 17 per cent. This occurred at 650°C.

In initial testing of the bench-scale equipment, Highvale coal was heated under flash hydropyrolysis conditions at a pressure of 10.8 MPa, a temperature of 800°C and a coal feed rate ranging from 0.4 to 2 kg/h. Under these conditions, the conversion rate varied from 23 to 53 per cent. The effects of pyrolysis versus hydropyrolysis and other reaction conditions on conversion rate were determined. It was observed that conversion rates were higher for hydropyrolysis reactions than for pyrolysis runs, and more hydrocarbon liquids were produced under high-pressure hydrogen than high-pressure helium.

Subsequently, the effects of various hydropyrolysis reaction conditions on the yield and quality of liquid products derived from Highvale coal were measured at 600 to 800°C, with pressures of 3.5 to 11 MPa

Entrained-Flow Pyrolysis Reactor System



(Source: Final Report on Pyrolysis Program: Phase I. Laboratory Evaluation on Pyrolysis Properties of Alberta Thermal Coal Regions, Knill, K., A.K. Chambers, S.K. Gangwal and J. Mendiuk, 1984)

and residence times of 0.5 to 5.8 seconds. Under these conditions, coal was converted to various solid, liquid and gaseous products. On a dry, ash-free basis, conversions were reported as follows:

Char: 37 to 74 per cent;

Tar: 3.2 to 20 per cent;

Benzene, toluene and xylene: 0 to 7 per cent;

Methane: 1 to 15 per cent;

Ethane: 0 to 6 per cent;

Hydrocarbon gases (C_3 and higher): 0 to 2 per cent;

Carbon oxides: 6 to 12 per cent; and

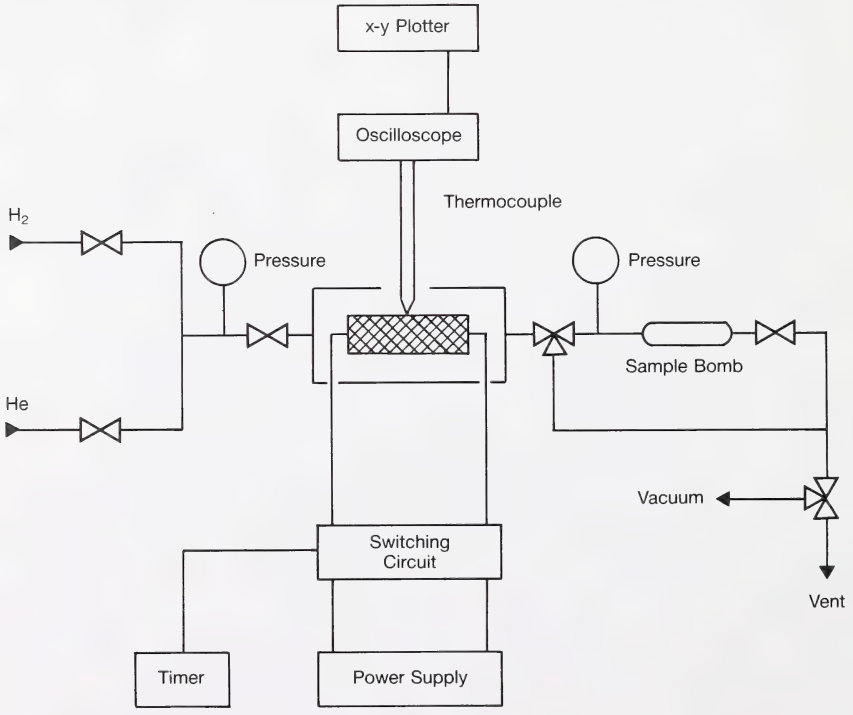
Water: 4 to 18 per cent.

To determine the kinetics of pyrolysis and hydropyrolysis reactions, a heated-screen device was designed that could be heated inductively at rates up to 1 000°C/s to temperatures as high as 1 000°C and for residence times from 0.1 to 60 seconds. Gas pressure could be varied from 0 to 10.3 MPa, and either inert helium or hydrogen gas could be used. A thermocouple in contact with the screen and monitored with an oscilloscope provided a time-temperature history of the reaction. Evolved gases were analyzed with a gas chromatograph and coal conversion was determined gravimetrically. An initial first order kinetic model was developed for the pyrolysis of coal at atmospheric pressure.

The solid hydropyrolysis char produced at temperatures higher than 650°C was highly porous and depleted of hydrogen, oxygen and sulphur. For most coals, the heating value of the char was greater than that of the parent, as-received coal. Removal of moisture and oxygen functionalities from the coal is responsible for this increase in heating value.

Measurements indicated that char represented 50 to 60 per cent of the products of pyrolysis. Because heating-value tests showed this material was a promising fuel for utility boilers, some combustion studies were carried out on

Heated Screen Reactor System



(Source: Final Report on Pyrolysis Program: Phase I. Laboratory Evaluation on Pyrolysis Properties of Alberta Thermal Coal Regions, Knill, K., A.K. Chambers, S.K. Gangwal and J. Mendiuk, 1984)

hydropyrolysis chars made from Highvale coal to obtain some indication of the manner in which these chars would behave under full-scale combustion conditions. Also, experimental procedures were developed to measure the porosity of coals because this characteristic is important for understanding the behaviour of coal in a variety of chemical reactions.

During 1985/86, the pyrolysis program was extended to include a greater combustion research effort aimed at measuring the combustibility characteristics of coals and chars. The highlights of this research are described in the technology transfer publication "Some Combustion Studies of Alberta Coals."

Supporting Investigations

Petrography, which is a method of classifying coals by their organic and mineral constituents, as well as reflectance, was used to characterize subbituminous coals from 13 coal regions to determine how coal components called macerals were influencing the liquefaction results. Also, the technique was used to characterize the products of coal liquefaction. Analysis of the results showed that all of the liptinite maceral was converted during liquefaction, while most of the vitrinite and some of the inertinite were converted. Knowing the maceral content of individual coals, however, did not allow precise predictions to be made about liquefaction behaviour.

In addition to petrography, various instrumental techniques were developed to help understand the chemistry of coal liquefaction and pyrolysis. They also permitted analysis of smaller samples than could be analyzed by traditional test methods. This involved the use of techniques such as thin-layer chromatography with flame-ionization detection, nuclear magnetic resonance, electron spin resonance, gas chromatography, gel permeation chromatography and mass spectrometry. These techniques were used to characterize asphaltenes and preasphaltenes, and oxygen and nitrogen compounds. They were also used to distinguish many of the diverse chemical compounds found in coal and its liquefaction or pyrolysis products. This initial work was followed by a substantial body of analytical research which will be described in a future technology transfer publication.

Computer programs to develop mathematical models of coal conversion processes were initiated. Using bench liquefaction data, the kinetics of hydrogen consumption, hydrocarbon gas production and coal liquefaction were examined, and models were developed for isothermal and non-isothermal axially dispersed tubular reactors.

Some initial attempts were made to upgrade the products of coal liquefaction to refinery-acceptable feedstocks. Subsequent upgrading studies will be the subject of a separate technology transfer publication.

Supercritical Gas Extraction of Coal

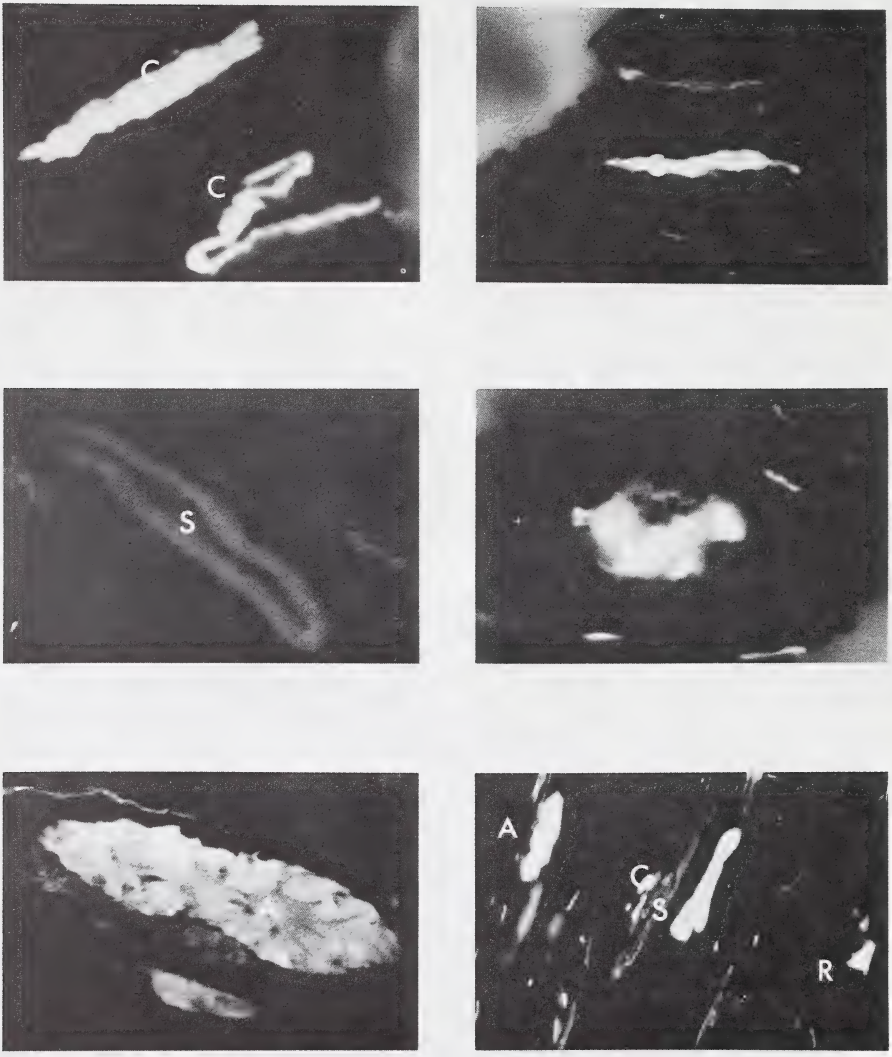
Although studies carried out at the Alberta Research Council showed that pyrolysis and hydropyrolysis processes could be used to produce liquid hydrocarbons from subbituminous coal, the yields of liquid products were low. An alternative method for extracting liquids from coal and producing a combustible solid involves supercritical gas extraction. This process is based on the fact that the vapour pressure of a solid or heavy liquid can be enhanced greatly by contacting it with a compressed gas.

Furthermore, extraction of coal with a suitable fluid at an appropriate temperature and pressure can remove non-volatile liquids which could not otherwise be recovered without extensive thermal treatment.

Consequently, a lignite from Saskatchewan and a high-volatile bituminous coal from Alberta were used in supercritical gas extraction studies at the University of Alberta. Water-saturated coal samples were reacted with steam and carbon monoxide under pressure (11.7 to 29.9 MPa) in a one-litre autoclave. Reactions were carried out at 400°C or 425°C. These temperatures were chosen to exceed the critical temperature of water (approximately 375°C) and the temperature at which active thermal decomposition of coal occurs (approximately 400°C). Catalysts were used in some of these experiments.

It was found that conversion to toluene-soluble "primary liquids" (plus co-produced water and gas) ranged from as high as 50 weight per cent in the case of lignite to 35 weight per cent for high-volatile bituminous coal. This was in the presence of a catalyst. When the catalyst was absent, the conversion rates were 42 and 27 weight per cent, respectively.

Subsequently, supercritical gas extraction was used on one lignite and four subbituminous coals. The latter coal rank was chosen because Alberta subbituminous coals do not respond well to low-temperature carbonization or flash pyrolysis processes. Also, it was thought that supercritical extraction might shed some light on the reasons that apparently similar subbituminous coals behave quite differently under certain treatment conditions.



Photomicrographs, in the fluorescence mode, of liptinite macerals: Alginite (A), Cutinite (C), Resinite (R) and Sporinite (S).

(Photomicrographs provided by Alberta Research Council)

Reactions were carried out in a one-litre stirred autoclave operated at temperatures of 400°C or 410°C and at pressures between 14 and 21 MPa. Conversion was defined as the sum of tar plus light hydrocarbons plus water and co-produced gas, and was expressed as a percentage of the dry, ash-free coal. Tars were analyzed by thin-layer chromatography for preasphaltenes, asphaltenes and "oils." Co-produced water was measured quantitatively, and analyses were performed on produced gases.

Extraction studies at 410°C and 14 MPa using either supercritical water and nitrogen, or supercritical water and carbon monoxide, showed that the presence of carbon monoxide in some instances increased the extraction yields by approximately 23 per cent and resulted in total conversion rates ranging from 30 to 44 per cent. These results were confirmed in the presence of iron oxide catalyst.

This enhancement resulted almost exclusively in a greater yield of light hydrocarbons, with little heavy and tar-like material. The yields of hydrocarbon liquids (tar plus light oil) were not related to coal rank or oxygen content, and the distribution of tar between preasphaltenes and asphaltenes was random. The produced gas was described as "hydrocarbon poor" and unlikely to be of interest. Also, the pressure of carbon monoxide reduced the formation of water derived from oxygen-bearing functional groups in the coal.

It was concluded that supercritical extraction resulted in hydrocarbon yields that were too small to be economically attractive. Even the best test conditions produced no more than 20 per cent tar and light oil. The study did demonstrate, however, that elemental and petrographic analyses do not provide enough information to explain the variable behaviour of similar coals. This subject is being pursued further in a separate investigation.

Liquefaction of Coal with Natural Gas

One of the drawbacks of conventional coal liquefaction processes is that they depend on the use of expensive hydrogen, which is usually added in the range of three to five per cent by weight of the coal feed. This is almost entirely molecular hydrogen, the production of which can account for one-third of the total operating costs of liquefaction processes.

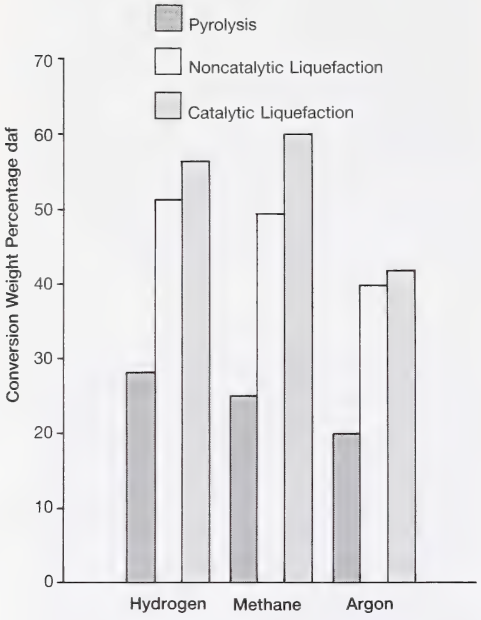
In this project, carried out at the University of Alberta, an alternative approach was tried. Instead of producing hydrogen from natural gas, which is commonly done now in Alberta, natural gas (methane) was used directly as the hydrogenation agent. This was done because abundant supplies of relatively inexpensive methane are available in Alberta. Also, methane is rich in hydrogen, and its chemistry suggested that it would not entail more severe reaction conditions than are used with molecular hydrogen.

In laboratory investigations using a specially designed micro-reactor, liquefaction or pyrolysis of Highvale subbituminous coal was carried out using tetralin as a donor solvent, and either methane or hydrogen as the hydrogenation gas. Runs with argon, an inert gas, were made to provide baseline conditions. For comparison, runs were also made with well-characterized Illinois #6 bituminous coal. All experiments were conducted at 450°C and 20 to 23.5 MPa. Some of the liquefaction experiments included Fe_2O_3 catalyst. The toluene-soluble fraction of the reaction products was used as a measure of the conversion rate. After toluene was distilled off, the products were analysed by elemental analysis, infra-red, gas chromatography and proton-nuclear magnetic resonance.

It was found that pyrolysis or liquefaction of Highvale coal in the absence of the catalyst resulted in higher rates of conversion for hydrogen than methane. However, when the Fe_2O_3 catalyst was present, the conversion to toluene-soluble products was higher with methane, or at least equal to that from hydrogen gas liquefaction. Also, liquefaction with natural gas produces more alkylated aromatic compounds and seven times the amount of C_2-C_5 gases than when hydrogen was used. This could lead to greater amounts of "light ends." In the case of Illinois #6 coal, both catalytic and non-catalytic reactions using methane resulted in higher conversion rates and more C_2-C_5 gases than with hydrogen.

It was concluded that substitution of natural gas for hydrogen could reduce the cost of producing liquid fuels and petrochemicals from coal.

Toluene-Soluble Conversions for Pyrolysis and Liquefaction of Highvale Coal with Hydrogen, Methane and Argon



(Source: Liquefaction of Coal with Natural Gas, Gray, M.R. and N.O. Egiebor, University of Alberta, November 1988)

Coal Conversion Waste Water Treatment

In the course of liquefying or gasifying coal, waste waters are produced that contain a wide variety and substantial quantities of organic compounds. These process effluents cannot be discharged into water bodies without first undergoing treatment to remove certain chemicals, the most prevalent and least desirable of which are menbers of the phenol family of compounds.

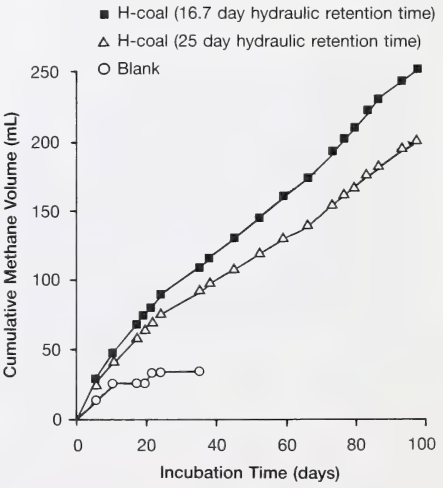
Research has indicated that anaerobic biological treatment may consume less energy and might be more cost-effective than the common aerobic methods of removing organic material from waste waters. In anaerobic processes, organic matter is converted by microbes to methane and carbon dioxide. The process involves two distinct groups of bacteria: methanogens and non-methanogens. To carry out complete anaerobic digestion of a substance, balanced growth of both types of bacteria must be maintained.

During initial studies at the University of Alberta, several phenols were exposed to anaerobically digested sewage sludge and the volume of methane produced was measured. It was found that some phenols could be converted to methane, but others passed through the process without changing. Similarly, when coal liquefaction waste water (obtained from the H-Coal piiot plant in Kentucky) was treated with anaerobic bacteria, it was found that only three types of phenols were converted to methane. Nonetheless, they represented approximately 85 per cent of the total phenols present in the waste water. It was also found that removal of phenolic compounds was inhibited by the presence of non-phenolic substances. Therefore, various methods for removing these substances in a cost-effective manner were explored. The approach selected eventually involved solvent extraction and pH control.

After the pH of coal liquefaction waste water was adjusted to between 7.0 and 11.5, the samples were solvent-extracted with di-isopropyl ether (DIPE) and exposed to nutrients and anaerobic digestion sludge for six weeks.

It was found that conversion of phenol to methane was no longer inhibited following solvent extraction by DIPE. This demonstrated that inhibitors were successfully removed.

Methane Production During Semi-continuous Fermentation of Extracted H-Coal Wastewater (Phases I and II)



(Source: Coal Conversion Wastewater Treatment Technology, Kindzierski, W.B., S.E. Hrudey and P.M. Fedorak, University of Alberta, 1988)

The results indicated that H-Coal waste water, extracted in the pH range of 8.5 to 10, would be free of inhibitors while consuming optimal quantities of pH-control chemicals.

Subsequently, waste water that had been solvent-extracted with DIPE at pH 9 was treated semi-continuously with anaerobic cultures. These experiments were successful.

Further Reading

Aitchison, D. and M.P. du Plessis. 1985. The Alberta Research Council's High Pressure Research Laboratory at Nisku. Canadian Chemical News 37:10-13.

Aitchison, D., P.D. Clark and L.K. Lee. 1985. Single-Stage and Two-Stage Liquefaction of Highvale and Vesta Coal in a Continuous Flow, Bench Scale Unit. Coal Research Department, Alberta Research Council. In: ENR-ARC Coal Conversion Research Program Final Reports for 1984/85, Volume I.

Berkowitz, N. 1981. Coal Chemistry - A Critical Status Review. Coal Research Department, Alberta Research Council. Report YCLQ-4.

Berkowitz, N. 1985. Supercritical Gas Extraction of Coal in an H-Donor System. Hydrocarbon Research Centre Inc., University of Alberta.

Berkowitz, N. and J. Calderon. 1987. On "Partial" Coal Conversion by Extraction with Supercritical H_2O. Fuel Processing Technology. 16: 245-256.

Berkowitz, N. and S. Steele. 1989. Extraction of Alberta Subbituminous Coals with Supercritical Water. University of Alberta.

Chakrabartty, S.K. 1981. Coal Pyrolysis: A State-of-the-Art Review. Coal Research Department, Alberta Research Council. Report YCPY-1.

Chakrabartty, S.K., J. Fryer and J. Campbell. 1981. Pyrolytic Properties of Alberta Coals. Coal Research Department, Alberta Research Council. Report YCPY-2.

Chakrabartty, S.K. and M.P. du Plessis. 1983. Evaluation of Alberta Plains Coals for Pyrolysis and Liquefaction Processes. Coal Research Department, Alberta Research Council. Report YCPY-7.

Chakrabartty, S.K. and M.P. du Plessis. 1985. Evaluation of Alberta Plains Coals for Pyrolysis and Liquefaction Processes. Coal Research Department, Alberta Research Council. Coal Report 85-1.

Chambers, A.K. 1982. Review of the Literature on Experimental Studies of the Pyrolysis and Hydropyrolysis of Coal. Coal Research Department, Alberta Research Council. Report YCPY-5.

Chambers, A.K., S.K. Gangwal and A.J. Royce. 1983. Pyrolysis and Hydropyrolysis of Alberta Subbituminous Coal Using the Heated Screen Apparatus. Coal Research Department, Alberta Research Council. Report YCPY-6.

Chambers, A.K., K.J. Knill, J. Dardis, J. Mendiuk, D. Ungarian, R. Zacharkiw and A. Kloc. 1985. Flash Hydropyrolysis and Char Combustion Studies of Alberta Coals. Coal Research Department, Alberta Research Council. In: ENR-ARC Coal Conversion Research Program Final Reports for 1984/85, Volume I.

Fedorak, P.M. and S.E. Hrudey. 1982. Anaerobic Methanogenic Treatment of Phenolic Wastewaters. University of Alberta.

Fedorak, P.M. and S.E. Hrudey. 1983. A Simple Apparatus for Measuring Gas Production by Methanogenic Cultures in Serum Bottles. Environmental Technology Letters. 4:425-432.

Fedorak, P.M. and S.E. Hrudey. 1984. The Effects of Phenol and Some Alkyl Phenolics on Batch Anaerobic Methanogenesis. Water Res. 18:361-367.

Fedorak, P.M. and S.E. Hrudey. 1986. Anaerobic Treatment of Phenolic Coal Conversion Wastewater in Semicontinuous Cultures. Water Res. 20:113-122.

Gangwal, S.K. and J. Mendiuk. 1983. Flash Pyrolysis/Hydropyrolysis of Alberta Subbituminous Coals: Design, Construction, Operation and Initial Results of a High Pressure 1-5 Kg/Hour Bench Unit. Coal Research Department, Alberta Research Council. Report YCPY-8.

Gawlak, M. and S.E. Moschopedis. 1981. Progress Report on the Autoclave Liquefaction Program for 1980-81. Coal Research Department, Alberta Research Council. Report YCLQ-1.

Gawlak, M., D. Carson, M. Holuszko and D. Vernon. 1982. Batch Autoclave Testing of Subbituminous Coals of Alberta: Carbon Monoxide/Steam and Dispersed Catalyst Process. Coal Research Department, Alberta Research Council. Report YCLQ-7.

Gawlak, M., D. Carson, N. Shatilla and H. Waslyk. 1983. Evaluation of Subbituminous Coals of Alberta: Reaction of Ardley, Judy Creek and Fox Creek with Carbon Monoxide and Steam. Coal Research Department, Alberta Research Council. Report YCLQ-26.

Gawlak, M., D. Carson, N. Shatilla and H. Waslyk. 1983. Evaluation of Subbituminous Coals of Alberta: Conversion of Ardley, Judy Creek and Fox Creek Coals in Dispersed Catalyst Process. Coal Research Department, Alberta Research Council. Report YCLQ-27.

Gibb, W.J., B. Ozum and M.P. du Plessis. 1982. Optimal Reactor Distribution with Fixed Terminal Constraints. Coal Research Department, Alberta Research Council. Report YCLQ-14.

Gray, M.R. and N.O. Egiebor. 1988. Liquefaction of Coal with Natural Gas. Department of Chemical Engineering, University of Alberta.

Hrudey, S.E. and P.M. Fedorak. 1984. Coal Conversion Wastewater Technology, Final Report. University of Alberta.

Iacchelli, A. and M. Selucky. 1983. Simulated Microdistillation of Coal-Derived Liquids by Thermogravimetry. Coal Research Department, Alberta Research Council. Report YCLQ-23.

Iacchelli, A. and M. Selucky. 1983. Proximate Analysis of Coal and Solid Products from Coal Conversion by Thermogravimetric Analysis. Coal Research Department, Alberta Research Council. Report YCLQ -24.

Kindzierski, W.B., S.E. Hrudey and P.M. Fedorak. 1988. Coal Conversion Wastewater Treatment Technology. University of Alberta.

Kindzierski, W.B., S.E. Hrudey and P.M. Fedorak. 1988. Solvent Extraction and Anaerobic Biological Treatment of a High Strength Phenolic Wastewater. Joint CSCE-ASCE National Conference on Environmental Engineering, July 13-15.

Kirchen, R., L. Lewkowicz, K. Badree, N. Shatilla and A. Stein. 1985. Coal Research Department, Alberta Research Council. In: ENR-ARC Coal Conversion Research Program Final Reports for 1984/85, Volume I.

Knill, K.J. 1982. Laboratory Scale Flash Pyrolysis of Alberta Subbituminous Coals. Coal Research Department, Alberta Research Council. Report YCPY-4. Knill, K.J., A.K. Chambers, S.K. Gangwal and J. Mendiuk. 1984. Final Report on Pyrolysis Program: Phase I. Laboratory Evaluation on Pyrolysis Properties of Alberta Thermal Coal Regions. Coal Research Department, Alberta Research Council. Report YCPY-12.

Kovacik, G. and B. Ozum. 1982. Rheological Characteristics of Coal Slurries. Coal Research Department, Alberta Research Council. Report YCLQ-17.

Lewkowicz, L., K. Badree, B. Ignasiak and M.P. du Plessis. 1983. Effect of Added H_2S or CS_2 on the Liquefaction of Alberta Subbituminous Coals in I.G. Farben and CO/Steam Process Types. Coal Research Department, Alberta Research Council. Report YCLQ-19.

Lewkowicz, L., K. Badree and B. Ignasiak. 1983. Behavioural Differences Between Two Solvents in Liquefaction of Alberta Subbituminous Coal with Hydrogen and Fe_2O_3 Catalyst. Coal Research Department, Alberta Research Council. Report YCLQ-28.

Lewkowicz, L., R. Lott, S.K. Chakrabartty and B. Ignasiak. 1984. Comparative Autoclave Liquefaction Studies of Alberta Subbituminous Coals - Final Report. Coal Research Department, Alberta Research Council. Report YCLQ-33.

Moschopedis, S.E., R.W. Hawkins and H. Wasylyk. 1981. Batch Autoclave Tests for the Liquefaction of Alberta Subbituminous Coals: I.G. Farben Liquefaction Process. Coal Research Department, Alberta Research Council. Report YCLQ-5.

Moschopedis, S.E. 1983. The Liquefaction of Alberta Subbituminous Coals: Batch Autoclave and Mini-Autoclave Tests. Coal Research Department, Alberta Research Council. Report YCLQ-32.

Moschopedis, S.E. and B. Ozum. 1984. Liquefaction Behaviour of Alberta Subbituminous Coals. Can. J. Chem. Eng. 62:374-377.

Oguztoreli, M.N., M.P. du Plessis and B. Ozum. 1983. Optimization of Coal Liquefaction Reactors. Can. J. Chem. Eng. 61:816-823.

Oguztoreli, M.N. and B. Ozum. 1983. Optimal Control of a Continuous Two Valves in Series Letdown Flow System. Can. J. Chem. Eng. 61:859-862.

Oguztoreli, M.N., M.P. du Plessis and B. Ozum. 1986. Heat Transfer in Axially Dispersed Two-Phase Flow Systems. Num. Heat Trans. 9:349-363.

Ozum, B. and M.P. du Plessis. 1982. Review of Heat Transfer and the Design of Heat Exchangers for Coal Slurries. Coal Research Department, Alberta Research Council. Report YCLQ-9.

Ozum, B., M.P. du Plessis and M.N. Oguztoreli. 1983. Optimization of Coal Liquefaction Reactors. Can. J. Chem. Eng. 61:816-823.

Ozum, B. 1985. Mathematical Modelling and Physical Parameters. Coal Research Department, Alberta Research Council. In: ENR-ARC Coal Conversion Research Program Final Reports for 1984/85, Volume I.

Ozum, B. 1985. Mathematical Modelling and Physical Parameters. Coal Research Department, Alberta Research Council. In: ENR-ARC Coal Conversion Research Program Final Reports for April 1 to September 30, 1985.

Ozum, B., S.E. Moschopedis, S.K. Chakrabarrty and M.N. Oguztoreli. 1985. On the Measurement of Coal Liquefaction Kinetics. Can. J. Chem. Eng. 63: 928-935.

Ozum, B., S. Parkash, S.K. Chakrabarrty and M.N. Oguztoreli. 1985. Mass Transfer Limitations in Coal Liquefaction. Liquid Fuels Tech. 3:229-249.

Ozum, B., M. Oguztoreli and M.N. Oguztoreli. 1987. Modelling of Axially Dispersed Non-isothermal Tubular Reactors for Hydroprocessing of Solid-Liquid Mixtures. Chem. Eng. Comm. 56:41-55.

Parkash, S., D. Carson and J. Soderlind. 1982. Rapid Heating Short Residence Time Liquefaction of Alberta Subbituminous Coals: Miniautoclave Tests. Coal Research Department, Alberta Research Council. Report YCLQL-11.

Parkash, S., M. Holuszko, C. Stangl, A.R. Cameron and M.P. du Plessis. 1982. Application of Coal Petrography in the Liquefaction of Subbituminous Coals and Lignites. Coal Research Department, Alberta Research Council. Report YCLQL-16.

Parkash, S., A.R. Cameron, W.D. Kalkreuth and M.P. du Plessis. 1983. Applied Coal Petrography - Part I: Application of Coal Petrography in the Liquefaction of Subbituminous Coals and Lignites. Coal Research Department, Alberta Research Council. Report YCLQ-21

Parkash, S., K. Lali, M. Holuszko and M.P. du Plessis. 1983. Contribution of Vitrinite Macerals to the Liquefaction of Subbituminous Coals. Coal Research Department, Alberta Research Council. Report YCLQ-20.

Parkash, S., K. Lali and M. Holuszko. 1984. Nature of Porosity in Alberta Subbituminous Coals. Coal Research Department, Alberta Research Council. Report YCPY-10.

Parkash, S. 1985. True Density and Elemental Composition of Subbituminous Coals. Fuel. 64:631-634.

Parkash, S., K. Lali, M. Holuszko and M.P. du Plessis. 1985. Separation of Macerals from Subbituminous Coals and Their Response to Liquefaction. Liquid Fuels Tech. 3:345-375.

Parkash, S., K. Lali and A.R. Cameron. 1985. Petrography of Subbituminous Coals from Alberta (Canada) Plains. J. Coal Quality. 4:84-91.

Parkash, S. 1985. Petrographic Characterization of Alberta Subbituminous Coals. Coal Research Department, Alberta Research Council. In: ENR-ARC Coal Conversion Research Program Final Reports for 1984/85, Volume I.

Parkash, S., K. Nesbitt and K. Lali. 1985. Fluorescence Microscopical Rank Studies on Sporinites (Liptinite Maceral) in Alberta Coal. Coal Research Department, Alberta Research Council. In: ENR-ARC Coal Conversion Research Program Final Reports for April 1 to September 30, 1985.

Sands, S.D. 1982. Liquefaction Characteristics of Highvale Coal in the Dow Coal Liquefaction Process. Coal Research Department, Alberta Research Council. Report YCLQ-18.

Selucky, M.L. 1985. ENR-ARC Coal Conversion Research Program Final Reports for 1984/85, Volume II Analytical R&D. Coal Research Department, Alberta Research Council.

Selucky, M.L. 1985. Analytical R&D. Coal Research Department, Alberta Research Council. In: ENR-ARC Coal Conversion Research Program Final Reports for April 1 to September 30, 1985.

Southern, T. and M. Selucky. 1983. Simulated Distillation by Gas Chromatography: Part I. Coal Research Department, Alberta Research Council. Report YCLQ-22.

Southern, T., W. Grochowski and M. Selucky. 1983. Correction Tables for the Conversion of Boiling Points Measured at Reduced Pressures to Their Atmospheric Equivalent Boiling Points. Coal Research Department, Alberta Research Council. Report YCLQ-31.

Southern, T., D. Cuthiell and M. Selucky. 1983. Novel Baseline Treatment in Simulated Distillation by Gas Chromatography, Final Report. Coal Research Department, Alberta Research Council. Report YCLQ-30.

Southern, T., D. Margel and M. Selucky. 1985. High Resolution Gas Chromatographic Analysis of Coal Derived Naphtha. Coal Research Department, Alberta Research Council. In: ENR-ARC Coal Conversion Research Program Final Reports for 1984/85, Volume I.

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Pub. No. I/300
ISBN 0-86499-651-9